PATENT COOPERATION TREATY

PCT 10/538200

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference S30490PCT	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/EP 03/10600	International filing date *(day/month/year)* 23.09.2003	Priority date *(day/month/year)* 12.12.2002
International Patent Classification (IPC) or both national classification and IPC C01B31/02		
Applicant SONY INTERNATIONAL (EUROPE) GMBH et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 7 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the opinion
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☒ Lack of unity of invention
   - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
28.05.2004	08.04.2005
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Marucci, A Telephone No. +49 89 2399-7819

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP 03/10600

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:

Description, Pages

1-33 as originally filed

Claims, Numbers

1-48 received on 22.03.2005 with letter of 22.03.2005

Drawings, Sheets

1/11-11/11 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☒ the claims, Nos.: 49-52
- ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

IV. Lack of unity of invention

1. In response to the invitation to restrict or pay additional fees, the applicant has:

   ☐ restricted the claims.

   ☒ paid additional fees.

   ☐ paid additional fees under protest.

   ☐ neither restricted nor paid additional fees.

2. ☐ This Authority found that the requirement of unity of invention is not complied with and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is

   ☒ complied with.

   ☐ not complied with for the following reasons:

4. Consequently, the following parts of the international application were the subject of international preliminary examination in establishing this report:

   ☒ all parts.

   ☐ the parts relating to claims Nos. .

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-48
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-48
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-48
	No:	Claims	

2. Citations and explanations

   see separate sheet

Re Item IV

Lack of unity of invention

1. The amendments filed with the letter of 22/03/2005 overcome the lack of unity objection raised previously during the search and examination procedure.

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1: US-B1-6 426 134 (LAVIN JOHN GERARD ET AL) 30 July 2002 (2002-07-30)

D2: HIRSCH, ANDREAS: "Functionalization of Single-Walled Carbon Nanotubes" ANGEW. CHEM. INT. ED., vol. 41, no. 11, 3 June 2002 (2002-06-03), pages 1853-1859, XP002241543

2.1 Claims 1 and claim 25 are concerned with a method for solubilizing carbon nanotubes by mixing them with urea and then heating.

Document D1 discloses a method for preparing single walled carbon nanotubes/polyurethane composites by contacting an amine derivatized nanotube with an isocianate and then by polymerizing (column 5, line 64-column 6, line 3).

Document D2 (section 5) discloses a method of solubilizing carbon nanotubes by derivatizing them.

Nowhere in these documents the possibility of using urea as a monomer precursor or as reactant to derivatize the nanotubes is disclosed (novelty in the sense of Art. 33(2) PCT).

2.2 The solubilization of carbon nanotube through the reaction of urea is therefore non-obvious and involves an inventive step in the sense of Art. 33(3) PCT:

2.4 The subject-matter of independent claims 40, 44 and 45 is also considered to be novel and inventive as the products herein disclosed are substantially different from the products obtained through the methods disclosed in D1 and D2.

2.5 Consequently, also the subject-matter of claim 58 and of the dependent claims 2-24, 26-39, 41-43, 46-57 are meeting the requirements of Art. 33(1) PCT.

3. Although claims 1 and 25 and claims 40, 44 and 45 have been drafted as separate independent claims, they appear to relate effectively to the same subject-matter and to differ from each other only with regard to the definition of the subject-matter for which protection is sought and in respect of the terminology used for the features of that subject-matter. The aforementioned claims therefore lack conciseness and as such do not meet the requirements of Article 6 PCT.

Claims

1. A method of solubilizing carbon nanotubes, comprising the steps:
   a) providing, in any order:
      carbon nanotubes, and
      at least one type of monomer molecules capable of undergoing a polymerization reaction or a precursor of the at least one type of monomer molecules;
   b) mixing together the nanotubes with the monomer molecules or their precursor;
   c) initiating a polymerization reaction of the monomer molecules
   to yield modified carbon nanotubes, wherein the carbon nanotubes have functional groups on their surface and/or ends, and wherein said polymerization reaction occurs at said functional groups.

2. The method according to claim 1, wherein the functional groups are oxygenated functional groups selected from the group comprising C-O species (alcohol, phenol, ether, epoxide), C=O species (aldehyde, ketone, quinone), and O-C=O species (carboxylic acid, ester, anhydride, lactone, pyrone).

3. The method according to any of the foregoing claims, wherein the carbon nanotubes are single-walled or multi-walled nanotubes.

4. The method according to any of the foregoing claims, wherein approximately 1 per 200 to 1 per 10 carbon atoms of the carbon nanotubes are in an oxidized state.

5. The method according to any of the foregoing claims, wherein approximately 1 per 150 to 1 per 20 carbon atoms of the carbon nanotubes are in an oxidized state.

6. The method according to claim 5, wherein approximately 1 per 100 carbon atoms of the carbon nanotubes are in an oxidized state.

7. The method according to any of the foregoing claims, wherein the monomer molecules are isocyanic acid and/or cyanate ion.

8. The method according to claim 7, wherein the precursor of the at least one type of monomer molecules is urea and/or its derivatives.

9. The method according to claim 7, wherein the precursor of the at least one type of monomer molecules is selected from the group comprising cyanuric acid, cyanuric chloride, isocyanuric acid and trichloroisocyanic acid.

10. The method according to claim 7, wherein the precursor is a cyanate salt.

11. The method according to any of the foregoing claims, comprising the additional step(s):
ba) heating the mixture, or, alternatively,
bb) acidifying the mixture or,
both steps ba) and bb).

12. The method according to claim 11, wherein the heating and/or acidifying is such, that the precursor of the at least one type of monomer molecules is induced to form said monomer molecules.

13. The method according to any of the foregoing claims, wherein the at least one type of monomer molecules or the precursor of the at least one type of monomer molecules is provided in a solvent.

14. The method according to any of the foregoing claims, wherein the carbon nanotubes are provided in a solvent.

15. The method according to claims 13 – 14, wherein the solvent of claim 15 is the same as the solvent of claim 14, or wherein the solvents are different.

16. The method according to any of claims 13 – 15, wherein the solvent(s) can be heated to a temperature close to or above the melting point of the monomer or its precursor, without decomposing.

17. The method according to any of the foregoing claims, wherein, before, during or after the polymerization reaction, at least one aldehyde is added to the mixture.

18. The method according to claim 17, when dependent on claim 11, wherein the at least one aldehyde is added during step ba).

19. The method according to any of claims 17-18, wherein the at least one aldehyde is selected from the group comprising acetaldehyde, benzaldehyde, carboxybenzaldehyde, cinnamaldehyde, chlorobenzaldehyde, ferrocene carboxaldehyde, formaldehyde, furfural, glutaraldehyde, paraformaldehyde, polyhydroxyaldehyde, propionaldehyde, pyridine aldehyde, salicylaldehyde and valeraldehyde.

20. The method according to claim 19, wherein the benzaldehyde is substituted with at least one electron-donating group, selected from -NHR, -NRR', -OH, -OR, $-C_6H_5$, $-CH_3$, $-CH_2R$, $-CHR_2$ and CR_3, wherein R and R' represent linear or branched C_1-C_{12} alkyl groups, C_3-C_8 cycloalkyl groups, C_6-C_{12} aralkyl groups, C_6-C_{12} aryl groups, poly(ethylene oxide), poly(propylene oxide), and poly(ethylene oxide)-co-poly(propylene oxide)block co-polymers.

21. The method according to claim 20, wherein the at least one electron-donating group on benzaldehyde is in the para-position.

22. The method according to any of claims 20 - 21, wherein the at least one electron-donating group on benzaldehyde is -OH or -OR, wherein R represents a linear or branched C_1-C_{12} alkyl group, a C_3-C_8 cycloalkyl group, a C_6-C_{12} aralkyl group, a C_6-C_{12} aryl group, poly(ethylene oxide), poly(propylene oxide), or poly(ethylene oxide)-co-poly(propylene oxide)block co-polymer.

23. The method according to any of claims 17-22, wherein the at least one aldehyde is selected from the group comprising p-anisaldehyde, 4-propoxybenzaldehyde and 4-(hexyloxy)benzaldehyde.

24. The method according to any of the foregoing claims, wherein, after step c), non-reacted monomer and/or precursor is removed from the reaction.

25. The method according to claim 24, wherein the removal occurs by a salt precipitation step, and/or by centrifugation or filtration, each of both possibilities optionally followed by washing, and/or by size separation and/or adsorption, and/or by enzymatic degradation, and/or by selective burning and/or by plasma treatment.

26. The method according to claim 25, wherein the salt precipitation occurs by addition of a salt, preferably a perchlorate salt, the filtration occurs using a membrane filter having a pore size smaller than 1 μm but larger than 0,01 μm, the size separation and/or adsorption occurs by gel-filtration, and the enzymatic degradation occurs by means of urease.

27. The method according to any of the foregoing claims, wherein after polymerization an amine-reactive compound, such as carboxylic acid anhydride, is added and reacted with the modified carbon nanotubes.

28. The method according to any of the foregoing claims, wherein the modified carbon nanotubes are dissolved in aqueous solution or in alcoholic solution, preferably methanolic solution.

29. A method of solubilizing carbon nanotubes, comprising the steps:
    a) Providing, in any order:
        carbon nanotubes, and
        urea;
    b) mixing together the nanotubes and the urea;
    c) heating the mixture of b).

30. The method according to claim 29, wherein the carbon nanotubes are as defined in any of claims 1 – 6.

31. The method according to any of claims 29 – 30, wherein the heating is above the melting temperature of urea.

32. The method according to claim 31, wherein the heating is in the range of approximately 130°C – 180°C, preferably approximately 150°C – 170°C, more preferably approximately 150°C – 160°C, most preferably approximately 150°C.

33. The method according to any of claims 29 – 32, wherein the heating is for approximately 1 – 60 min, preferably approximately 3 – 20 min, more preferably approximately 5 – 15 min, most preferably approximately 10 minutes.

34. The method according to any of claims 29-33, wherein at least one aldehyde is added to the mixture of b).

35. The method according to claim 34, wherein the at least one aldehyde is added to the mixture of b) before or during step c).

36. The method according to claim 35, wherein the at least one aldehyde is added during step c), preferably 1-5 minutes after step c) has been initiated, most preferably 1-3 minutes after step c) has been initiated.

37. The method according to any of claims 34-36, wherein the at least one aldehyde is selected from the group comprising acetaldehyde, benzaldehyde, carboxybenzaldehyde, cinnamaldehyde, chlorobenzaldehyde, ferrocene carboxaldehyde, formaldehyde, furfural, glutaraldehyde, paraformaldehyde, polyhydroxyaldehyde, propionaldehyde, pyridine aldehyde, salicylaldehyde and valeraldehyde.

38. The method according to claim 37, wherein the benzaldehyde is substituted with at least one electron-donating group, selected from -NHR, -NRR', -OH, -OR, $-C_6H_5$, $-CH_3$, $-CH_2R$, $-CHR_2$ and CR_3, wherein R and R' represent linear or branched C_1-C_{12} alkyl groups, C_3-C_8 cycloalkyl groups, C_6-C_{12} aralkyl groups, C_6-C_{12} aryl groups, poly(ethylene oxide), poly(propylene oxide), and poly(ethylene oxide)-co-poly(propylene oxide)block co-polymers.

39. The method according to claim 38, wherein the at least one electron-donating group on benzaldehyde is in the para-position.

40. The method according to any of claims 38 - 39, wherein the at least one electron-donating group on benzaldehyde is -OH or -OR, wherein R represents a linear or branched C_1-C_{12} alkyl group, a C_3-C_8 cycloalkyl group, a C_6-C_{12} aralkyl group, a C_6-C_{12} aryl group,

poly(ethylene oxide), poly(propylene oxide), or poly(ethylene oxide)-co-poly(propylene oxide)block co-polymer.

41. The method according to any of claims 34-40, wherein the at least one aldehyde is selected from the group comprising p-anisaldehyde, 4-propoxybenzaldehyde and 4-(hexyloxy)benzaldehyde.

42. The method according to any of claims 29 – 41, wherein the product of step c) is dissolved in aqueous solution or alcoholic, preferably methanolic solution or a mixture of an aqueous and an alcoholic solution, and subjected to a salt precipitation step, and/or centrifugation or filtration, each of both possibilities optionally followed by washing, and/or subjected to size separation and/or adsorption and/or enzymatic degradation, and/or selective burning, and/or plasma treatment.

43. The method according to claim 42, wherein the product of step c) is dissolved in aqueous solution or alcoholic, preferably methanolic solution or a mixture of an aqueous and an alcoholic solution, and is subjected to an evaporation step.

44. A carbon nanotube, produced by the method according to any of claims 1 – 43.

45. The carbon nanotube according to claim 44, wherein the nanotube is non-bundled.

46. The carbon nanotube according to any of claims 44 – 45, wherein it is decorated in a pearl chain-like manner with discrete bodies, when viewed by AFM.

47. The carbon nanotube according to any of claims 44 – 45, having one or more physical characteristics selected from the group comprising:
- a solubility in water or aqueous solution of up to approximately 10 g/l and/or a solubility in methanol or methanolic solution of up to approximately 1 g/l,
- an absorption maximum between 210 nm and 250 nm,
- one or several or all of the following absorption maxima in the infrared in the following wavenumber regions:

3470 – 3490 cm^{-1}, 3420 – 3440cm^{-1}, 3365 – 3385 cm^{-1}, 3330 – 3350 cm^{-1}, 3245 – 3265 cm^{-1}, 3210 – 3230 cm^{-1}, 1660 – 1680 cm^{-1}, 1610 – 1630 cm^{-1}, 1450 – 1470 cm^{-1}, 1330 – 1350 cm^{-1} and 1095 – 1115 cm^{-1}.

48. An association of carbon nanotubes according to any of claims 46 – 47, wherein the carbon nanotubes are non-bundled, but interconnected at their ends through said discrete bodies into branched structures, when viewed by AFM.

49. A carbon nanotube or an association of carbon nanotubes produced by the method according to claim 43.

50. The carbon nanotube or association of carbon nanotubes according to claim 49, which is at least partially crystalline.

51. The carbon nanotube or association of carbon nanotubes according to any of claims 49 – 50, having one or more physical characteristics selected from the group comprising:
    - one or several or all of the following absorption maxima in the infrared in the following wavenumber regions:
      3370 – 3390 cm^{-1}, 3205 – 3225 cm^{-1}, 3060 – 3080 cm^{-1}, 1700 – 1720 cm^{-1}, 1680 – 1700 cm^{-1}, 1655 – 1675 cm^{-1},1580 – 1600 cm^{-1}, 1500 – 1520 cm^{-1}, 1440 – 1460 cm^{-1}, 1395 – 1415 cm^{-1}, 1245 – 1265 cm^{-1}, 1155 – 1175 cm^{-1}, 1020 – 1040 cm^{-1}, 845 – 865 cm^{-1}, 795 – 815 cm^{-1},
    - having both crystalline and amorphous parts, when viewed under AFM, TEM and/or SEM.
    - a solubility in water or aqueous solution of up to approximately 10 g/l and/or a solubility in methanol or methanolic solution of up to approximately 1 g/l.

52. Use of a carbon nanotube according to any of claims 44 – 47 or of an association of carbon nanotubes according to claim 48 or of a carbon nanotube or association of carbon nanotubes according to any of claims 49 – 51 in an electronic device, a nanoelectronic device, a memory element, a field emission device, a sensor, an actuator, an electromechanical device, a composite material, a coating/paint/paste, a hydrogen storage device, a battery or fuel cell, a supercapacitor, a photoelectrochemical device, a photovoltaic device,

an energy conversion device, a light emitting diode, a liquid crystal display, a probe scanning probe microscopy, a non-linear optical device or antenna, or a catalyst.